Synthetic and Mechanistic Chemistry

Security at center of chemical and mechanistic chemistry research at Lab

Project Description

Los Alamos scientists are using synthetic and mechanistic chemistry to address energy security and other emerging challenges, including global security and core weapons missions.

Synthetic chemistry includes work in ligands for catalysts, fission-products separations for isotope delivery, and labeled substrates for reaction mechanisms.

Other research addresses materials synthesis for energy applications.

Examples include

- nanoparticle synthesis for quantum dots
- light- and energy-harvesting inorganic/nanoparticulate/molecular constructs
- inorganic materials to study radioparagenesis relevant to nuclear waste forms
- ionic liquids for actinide dissolution and deposition

Capabilities

Developing synthetic materials and catalysts for energy applications and mechanistic chemistry for biofuel production.

Designing a variety of biomedical technologies, including (1) active coatings for waveguides in sensing technologies and (2) new ligand environments to conduct diagnostic and therapeutic isotope delivery in support of isotope science.

Using nanoparticles in applications that range from energy to scintillator devices.

Performing weapons chemistry of targets for cross-section measurements, energetic ligands, and composites.

Conducting separations for (1) medical isotope purification and (2) nuclear fuel cycles.

Performing the mechanistic chemistry of radiation-induced transformations.

Applying radiological signatures to national security applications.

Research and Technology Development Areas

- Performed research that may make it possible to replace traditionally used noble metal catalysts with cobalt. A common metal, cobalt holds promise as an industrial catalyst with potential applications in energy-related technologies, such as the production of biofuels and the reduction of carbon dioxide. That is, provided the

cobalt is captured in a complex molecule so it mimics the previous metals that normally serve this industrial role. This work was published in the international edition of the chemistry journal *Angewandte Chemie.* [http://www.lanl.gov/newsroom/news-releases/2012/November/11.26-hanson-catalysis.php]

- Made advances in opening hydrocarbon rings in biomass-derived furan. Recent work investigates a method of opening biomass-derived furan rings under mild conditions and holds promise for converting biomass into liquid hydrocarbons. This area of research is fast moving and presents an opportunity to decrease dependence on fossil fuels and move toward a more carbon-neutral fuel economy. For use in transportation, there are currently several strategies being considered to create liquid fuel from different biomass feedstocks [http://pearl1.lanl.gov/external/Research/ring-opening-article.shtml].
- Successfully demonstrated the production and separation of molybdenum-99 (Mo-99) from uranium sulfate solution using a separation flow sheet designed by Argonne National Laboratory. This work is supported by the Department of Energy's National Nuclear Security Administration's Global Threat Reduction Initiative and was preformed for SHINE Medical Technologies, Inc. which will produce the medical radioisotope. [http://wisconsintechnologycouncil.com/newsroom/?ID=1924].
- Fabricated transparent thin films capable of absorbing light and generating electric charge over a relatively large area. The material, described in the journal *Chemistry of Materials*, could be used in development of transparent solar panels [http://www.lanl.gov/newsroom/news-releases/2010/November/11.03-transparent-light-harvesting-material.php].
- Used genetic engineering to develop magnetic algae, thus making it much easier to harvest for biofuel production. Part of this effort involved taking a gene known to form magnetic nanoparticles in magnetotactic bacteria and expressing it in green algae. Harvesting algae accounts for approximately 15–20 percent of the total cost of biofuel production—magnetic algae can reduce such costs by more than 90%.
- Developed conducting polymer (polyaniline) thin films as substrates that grow nanostructured silver nanoparticles. The nanoparticles can be used for surface enhanced Raman spectroscopy (SERS) for molecular sensing applications. The new films grow metal nanoparticles with tunable morphologies not achievable by more traditional solution-based synthetic approaches. Such tunability is achieved by manipulating experimental conditions such as temperature and concentration, and by varying the reduction potential of the polyaniline films through doping. Varying the reduction potential of the films enables the spontaneous deposition of silver (or other metals) on the polymer surface from an aqueous solution of metal ions. Scientists have demonstrated a range of nanostructured features that can be controllably and reproducibly formed over any shape in which the polymer has been formed.
- Applied a new nanoscale spectroscopic technique (known as a "nanoscale flashlight") to study the collective oscillations of electrons in individual gold nanoparticles and their assemblies. A deeper understanding of these oscillations and their interactions will not only provide a foundation for research in the new and emerging field of nanoplasmonics, but it may have practical applications in the ultrasensitive detection of chemical and biological molecules.
- Using organometallic chemistry to investigate actinide-ligand covalent interactions. Such chemistry provides exquisite synthetic control and offers a breadth of structural motifs. The goal of this project is to understand the nature of chemical

bonding and the relative roles of valence 5*f* and 6*d* orbitals through reaction chemistry. We also wish to explore manifestations of covalent metal-ligand bonding in complexes of uranium and the other light actinides over a broad range of ligand sets and structure types. We will carry out such investigations by combining synthetic organometallic chemistry, electronic structural characterization, and density functional theory.

- Performing synthetic and experimental chemistry of high explosives. New synthetic protocols have yielded numerous types of explosives, from high-nitrogen high explosives that produce primarily nitrogen gas upon detonation to lead-free primaries and nano-aluminum-containing high explosives with improved detonation properties. Related research has produced offshoots such as metal nanofoams (R&D 100 winner in 2005), super-thermite electric matches (R&D 100 winner in 2003), and advances in plastics chemistry.
- Using self-assembly coupled with synthetic chemistry techniques to functionalize silica materials with reactive binding sites. Current projects include the functionalization of silica materials to immobilize active proteins to conduct characterization studies or develop sophisticated sensors. Other projects involve the synthesis of functional silica nanoparticles for various sensing and tracking applications.

LANL Facilities and Resources

Center for Integrated Nanotechnologies: Scientists at this center develop the scientific principles that govern the design, performance, and integration of nanoscale materials.

Key Personnel

- Jurgen G. Schmidt: Synthetic chemistry and stable isotopes for biological applications
- Aaron S. Anderson: Synthetic chemistry of biosensors
- Andrew M. Dattelbaum: Synthetic chemistry and nanoparticles

Sponsors, Funding Sources, or Agencies

Department of Energy's National Nuclear Security Administration's Global Threat Reduction Initiative

Awards

- 2005 R&D 100 Award for nanoFOAM
- 2003 R&D 100 Award for Super-Thermite Electric Matches

Publications

Ruilian Wu, Siegfried N. Lodwig, Jurgen G. Schmidt, Robert F. Williams, and Louis A. Pete Silks, "Synthesis of 13C labeled sulfur and nitrogen mustard metabolites as mass spectrometry standards for monitoring and detecting chemical warfare agents" *Journal of Labelled Compounds and Radiopharmaceuticals* 55(6), 211–222

Harshini Mukundan, Dominique N. Price, Matthew Goertz, Ramakrishnan Parthasarathi, Gabriel A. Montaño, Sandeep Kumar, Matthew R. Scholfield, Aaron S. Anderson, S. Gnanakaran, and Srinivas Iyer, et al., "Understanding the interaction of Lipoarabinomannan with membrane mimetic architectures," Tuberculosis 92(1), 38–47

Tiziano Gaiotto, Hau B. Nguyen, Jaemyeong Jung, Gnana S. Gnanakaran, Jurgen G. Schmidt, Geoffrey S. Waldo, Andrew M. Bradbury, and Peter M. Goodwin, “A photophysical study of two fluorogen-activating proteins bound to their cognate fluorogens,” Progress in Biomedical Optics and Imaging - Proceedings of SPIE, 7905 (2011).

Jennifer L. S. Sporty, Sharon W. Lemire, Edward M. Jakubowski, Julie A. Renner, Ronald A. Evans, Robert F. Williams, Jurgen G. Schmidt, Marcel J. Van Der Schans, Daan Noort, and Rudolph C. Johnson, “Immunomagnetic separation and quantification of butyrylcholinesterase nerve agent adducts in human serum,” Analytical Chemistry 82(15), 6593–6600 (2010).

J. Gabbard, N. Velappan, R. Di Niro, J. Schmidt, C.A. Jones, S.M. Tompkins, and A.R.M. Bradbury, “A humanized anti-M2 scFv shows protective in vitro activity against influenza,” Protein Engineering, Design and Selection 22(3), 189–198 (2009).

Ramesh R. Kale, Harshini Mukundan, Dominique N. Price, J. Foster Harris, Daniel M. Lewallen, Basil I. Swanson, Jurgen G. Schmidt, and Suri S. Iyer, “Detection of intact influenza viruses using biotinylated biantennary S-sialosides,” Journal of the American Chemical Society 130(26), 8169–8171 (2008).

Aaron S. Anderson, Andrew M. Dattelbaum, Gabriel A. Montano, Dominique N. Price, Jurgen G. Schmidt, Jennifer S. Martinez, W. Kevin Grace, Karen M. Grace, and Basil I. Swanson, “Functional PEG-modified thin films for biological detection,” Langmuir 24(5), 2240–2247 (2008).

Harshini Mukundan, Sandeep Kumar, Dominique N. Price, Sonja M. Ray, Ye-Jin Lee, Seonyeong Min, Seokyong Eum, Jessica Kubicek-Sutherland, Jesse M. Resnick, and W. Kevin Grace, et al., “Rapid detection of Mycobacterium tuberculosis biomarkers in a sandwich immunoassay format using a waveguide-based optical biosensor,” Tuberculosis 92(5), 407–416 (2012).

Harshini Mukundan, Hongzhi Xie, Dominique Price, Jessica Z. Kubicek-Sutherland, W. Kevin Grace, Aaron S. Anderson, Jennifer S. Martinez, Nile Hartman, and Basil I. Swanson, “Quantitative multiplex detection of pathogen biomarkers on multichannel waveguides,” Analytical Chemistry 82(1), 136–144 (2010).

Harshini Mukundan, Aaron S. Anderson, W. Kevin Grace, Karen M. Grace, Nile Hartman, Jennifer S. Martinez, and Basil I. Swanson, “Waveguide-based biosensors for pathogen detection,” Sensors 9(7), 5783–5809 (2009).

More publications